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UNDERSTANDING METHANOL FORMATION IN PULP MILLS

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ABSTRACT

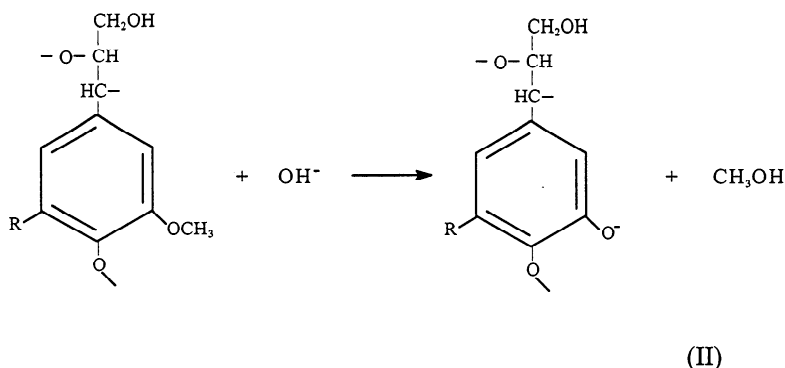
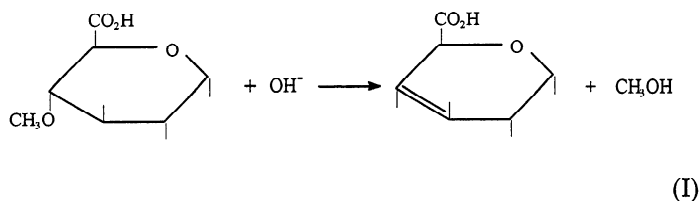
Methanol emission in pulp mills has been an environmental concern. The Cluster Rule now requires the control of methanol emission in pulp mills. We conducted laboratory pulping studies in a batch digester to quantify the methanol formation during pulping. Based on our laboratory experiments, we found that about 75% of the methanol formed in the pulping processes are due to the rapid and completed alkaline hydrolysis reaction of 4-O-methylglucuronic acid residues in hemicellulose (or demethylation of xylan) and lignin demethylation only accounts for less than 20% of the methanol in the spent pulping liquor. We also found from experiments that methanol can be formed during the evaporation of weak black liquor and in the black liquor storage tanks. The methanol formation in these two systems is mainly due to the slow reaction of lignin demethylation. The results indicated that 99% of the methanol including those in the original liquor plus those formed in the evaporation leave the concentrated black liquor after the liquor solids content reaches about 20% and, therefore, can be collected during evaporation. In this paper, we present the results obtained from our laboratory study along with the implications to mill operations.

INTRODUCTION

The formation of volatile organic compounds (VOCs), such as methanol, in kraft mills has been an environmental concern. Methanol is soluble in water and can increase the biochemical oxygen demand (BOD). Furthermore, it can also be released into the atmosphere at the process temperatures of kraft mill streams. The cluster rule [1] now requires control of the release of methanol in pulp and paper mills. Unfortunately, knowledge of methanol formation in pulp and paper manufacturing processes is very limited. Methanol is primarily produced through the pulping process in digesters. In a recent study [2], we reported that methanol formation during pulping is mainly due to the rapid demethylation of wood xylan. Many mills have reported that methanol can also be formed in black liquor evaporators and storage tanks. However, the mechanisms of methanol formation in these two systems have not been identified and the amount of methanol formed has not been quantified.

Based on the studies reported in the literature [3-5], there are two general accepted mechanisms of methanol formation in pulping processes: the hydrolysis of xylan, i.e., the rapid alkaline hydrolysis reaction of 4-O-methylglucuronic acid residues in hemicellulose [3] to form hexeneuronic acid groups and methanol, and the demethylation of lignin [4, 5]. These two mechanisms can be described by the chemical reactions (I) and (II), respectively, shown below. According to Sarkanen et al. [5], the amount of methoxyl groups on lignin that can be demethylated is very small. Therefore, it is reasonable to assume that the majority of methanol is formed through the demethylation of xylan [3, 5] in pulping. Based on this argument, we conducted a methanol mass balance analysis in our previous study [2] and found that 100% demethylation of xylan accounts for about 75% of the total

methanol formed in our laboratory batch pulping processes based on our experimental data. Lignin demethylation accounts for 20% of the total methanol formed. With the assumption of complete hydrolysis of the xylan methoxyl groups to form methanol in the pulping process, the only pathway for methanol formation from subsequent black liquor processes (storage and evaporation) is by lignin demethylation.



In this study, we conducted various laboratory batch pulping processes, laboratory batch black liquor evaporation experiments, and investigated the methanol formation in black liquor samples stored in isothermal conditions. It is the intention of the present study to use the laboratory data to explain methanol formation in pulp mills.

EXPERIMENTAL

Pulping

In a previous study [2] only conventional kraft and soda pulping processes for bleach grade pulps were carried out. In this research, methanol formation in different pulping processes was studied. For each set of pulping conditions selected, the pulping process was terminated at a different pulping time to obtain the rate of formation of methanol under a selected set of pulping conditions. By this approach, the effect of pulp kappa number or cooking H factor on methanol formation can be obtained. All the pulping work was conducted in a bomb digester of volume 500 mL. Each cook used 50 grams of oven-dry wood chip. Methanol concentrations in the pulping spent liquors were analyzed using the method we developed previously [6] on a commercial Headspace Gas Chromatograph (HSGC, HP-7694 and HP-6890 Hewlett-Packard, Palo Alto, CA).

Black Liquor Storage

As we indicated in the previous section, methanol formation in the post pulping black liquor processes is due to lignin demethylation. To understand methanol formation during black liquor storage, we conducted two sets of experiments. The chemicals used in the first set of experiments were commercial grade softwood lignin and

hydroxide solution. Weak black liquor was used in the second set of experiments. For each set of experiments, the chemicals were put in a sampling vial of volume 20 mL. The vial was heated at various temperatures by an isothermal oven of a commercial Automated Headspace Sampler (HP-7694, Hewlett-Packard, Palo Alto, CA) to simulate black liquor storage process in a constant temperature environment. Multiple headspace extractions from the vial at an interval of 60 minutes were carried out for each sample at a given temperature. The headspace sampler was connected to a GC for methanol analysis. It is assumed that the amount of methanol vapor extracted out for GC measurement in each headspace extraction was very small and ignored compared to the total methanol in the liquid because the methanol vapor concentration in the headspace is very low.

Black Liquor Evaporation

Laboratory batch black liquor evaporation experiments were conducted using an isothermal bath. The isothermal bath uses polyethylene glycol (PEG) as heating medium. The flashing point of PEG is 149°C. Figure 1 shows a schematic of the batch evaporator that consists of a homemade boiler of capacity 100 mL, distillation column that was set up vertically to prevent the overflow of foaming liquor due to heating. The distillation column was heated using a heating tape to prevent condensation on the wall. The vapor was condensed in a graduated cylinder (as a receiver) that is cooled by an ice bath. The volume of the condensate can be easily read from the scale on the cylinder and recorded during experimentation. The temperature of the PEG was controlled using a temperature controller to obtain a constant heat flux to the boiler. The same amount of 50 mL black liquor was used for each batch experiment. Several batch evaporation experiments were carried out. The duration of each batch evaporation was varied to obtain the time dependent methanol formation and vaporization data. The starting liquor composition, solids, etc. are the same as they are taken from the same source. The HSGC described above was used for methanol analysis. It should be noted that the batch black liquor evaporator is different from the evaporators used in mills. Cares should be taken in using the data obtained in the present study to explain mill methanol formation during evaporation.

RESULTS

Methanol Formation During Pulping

Based on our previous laboratory pulping study [2], we have concluded that 75% of the methanol was formed during pulping by the 100% hydrolysis of xylan. Lignin demethylation contributes 20% of the methanol formed in pulping. The effects of kappa number of pulping process on methanol formation were studied in this research. We conducted conventional kraft pulping with and without catalyst AQ at two different sulfidities, soda pulping, polysulfide pulping with and without AQ at two different sulfidities, and a multistage pulping to simulate a RDH process. For each pulping process selected, several batch cookings were conducted that were terminated at different cooking times to obtain desired kappa number. Only southern pine was used in the present study. Pulp yield, kappa number, and methanol concentration in the pulping spent liquors were analyzed.

Figure 2 shows the results of methanol formation per ton of oven-dry pulp calculated based on the measured quantities. The results confirmed our previous study [2] that the effect of pulping process and catalyst AQ on total methanol formation is not very significant. The data show that the total methanol formed per ton of oven-dry pulp is a strong function of pulp kappa number or H factor, indicating the effect of ongoing xylan hydrolysis and lignin demethylation reactions on methanol formation. The scatter of data is partly due to the actual small variations of pulping processes and partly due to measurement errors. The fact that the data scatter in Fig. 2b is not as severe as in Fig. 2a indicates that methanol formation reactions (I) and (II) are strongly affected by the cooking H factor (total

energy input), or temperature. The data also show that about 8.5 and 7.0 kg/ODT pulp methanol will be formed in the pulping of bleach grade ($\kappa = 30$) and liner board grade ($\kappa = 70$) southern pine, respectively. These numbers agree with those reported at various mills in the US [7]. The fact that the pulping process does not have a significant effect on methanol formation indicates that rapid and complete hydrolysis of xylan is the major pathway for methanol formation. Measurements of hexeneuronic acid (HUA) groups formed by xylan hydrolysis (Reaction I) show that the amount of HUA found in pulps obtained under similar pulping experiments was linearly proportional to the methanol concentration in the pulping spent liquor up to 75% of the concentration level [8], which further validates the above conclusion.

For practical application purposes, we conducted a regression analysis to obtain the following equations for the prediction of methanol formation during pulping.

$$m_{MeOH}(kg / ODTPulp) = 10.09 - 0.0311 \kappa - 0.00017 (\kappa)^2 \quad (1)$$

$$m_{MeOH}(kg / ODTPulp) = 0.644 \cdot (HFactor)^{0.368} \quad (2)$$

It should be pointed out that the above two equations are simply a mathematical fit of the data. The equations neglect the effects of AQ, sulfidity, and other pulping parameters and were obtained for southern pine only. It is intended for qualitative prediction only. The actual experimental data are needed to be used for accurate applications.

Methanol Formation During Black Liquor Storage

Model System

Laboratory simulation experiments using caustic solution with alkali softwood lignin in an isothermal environment were conducted at several temperatures. Both the lignin and hydroxide concentrations were varied. The results indicate that methanol can be formed through the demethylation of lignin as shown in Fig. 3, though the lignin demethylation is very slow. We also found that the methanol formation is linearly proportional to the lignin mass concentration in the caustic solution as shown in Fig. 4. However, the effect of the hydroxide concentration on methanol formation is less significant (compared with lignin) as shown in Fig. 5, in particular at high pH values. Because the pH of black liquor is around 12.5-13.5, we can conclude that the effect of hydroxide concentration on methanol formation is not significant. Based on the data presented in Figs. 3-5, we obtained the following kinetic expression for qualitative prediction of methanol formation rate in black liquor storage,

$$\frac{dC_{MeOH}}{dt} = Z \cdot \exp\left(-\frac{E}{RT}\right) \cdot (C_{lig}^0)^a \cdot (C_{OH^-}^0)^b \quad (3)$$

where $Z = 1062.5$, $E = 2.6822 \times 10^7$, $a = 1.0$, and $b = 0.1$. C_{lig}^0 and $C_{OH^-}^0$ are the initial lignin mass and hydroxide mole concentration, respectively.

Black Liquor

To verify the results obtained using model systems of hydroxide and lignin solutions, we conducted similar experiments using black liquors obtained in our pulping studies. Two black liquors were used from two batch conventional kraft cooks with AA = 15% and sulfidity = 15%. The final pulp kappa numbers of the two cooks are 59 and 104, respectively. Experiments were conducted to investigate the methanol formation from these two liquors under two isothermal conditions. It was found that the methanol formation rate was very slow and increased as the reaction temperature was increased as shown in Fig. 7, which agrees with the results obtained using model systems.

Unlike the model system that the methanol concentration in the caustic solution increased linearly with time, the methanol concentration in black liquor storage levels out about 6 hours in the experiments. It is unclear at this time whether a chemical equilibrium has been reached or not in the reactor so that methanol concentration will no longer increase after 6 hours. Or simply the lignin demethylation reaction has stopped. The amount of methanol formed was about 10% of that in the original liquor. With the limited data we have for the two temperatures, it is not clear whether or not the lignin demethylation reaction end point varies with reaction temperature.

We also compared the methanol formation results from two liquors used. As shown in Fig. 8, the methanol formation rate was higher in the liquor that corresponds to the pulp with a high kappa number ($\text{kappa} = 104$) than the liquor with a low kappa number ($\text{kappa} = 59$). This seems to contradict Eqn. (3) obtained from model systems because the liquor with high kappa has a low lignin concentration and the liquor with low kappa has a high lignin concentration. However, the overall methanol formation from the liquor with low kappa is greater than that from the liquor with high kappa. To explain this phenomenon, we also compared the results from the liquor with pulp $\text{kappa} = 104$ with the data obtained from a model system shown in Fig. 3. The comparison as shown in Fig. 9 indicates that the methanol formation in the black liquor with pulp $\text{kappa} = 104$ was higher than that in a model system with lignin concentration of 6% and hydroxide concentration of 0.6 mole/L (or $\text{pH} = 13.6$). The most probable explanation for this is due to the differences of the lignin structure. Liquors derived from high kappa pulping is most likely to contain lignins of low molecular weight that are easy to react with hydroxide, therefore, the lignin demethylation reaction rate is expected to be higher than that in liquors derived from low kappa pulping. Because the liquors derived from low kappa pulping contain higher lignin content due to further delignification than liquors derived from high kappa pulping, it is expected that the final methanol concentration in liquors from low kappa pulping will be high. Commercial grade lignin used in the studies of model systems was obtained from the wash of black liquors. The lignin tends to contain a large amount of high molecular weight lignin because typical pulp kappa numbers for bleach and liner grade pulps are 30 and 70, respectively, for softwood, which cause the low methanol formation rate. Further study on the subject is required to understand the fundamentals of lignin demethylation.

The above results indicate that methanol formation in black liquor storage will be significant in a mill environment that has a typical black liquor retention time of a couple of days even though the lignin demethylation reaction is very slow. The amount of methanol formed is less affected by the pH of the liquor but will be affected by the lignin content of the liquors.

Methanol Formation During Black Liquor Evaporation

Laboratory batch evaporation experiments of a kraft liquor collected from a unbleached mill with an initial solids content of 5% were conducted to study methanol formation during liquor evaporation through lignin demethylation. Methanol concentrations in the boiler liquor and in the receiver condensate were analyzed for each batch evaporation. Material balance of methanol was carried out. The results are shown in Fig. 10. It was found that a significant amount of methanol (about 300%) was formed during concentration of the liquor from 5% to about 30% total solids. In Fig. 10, it also shows that most of methanol (original in the liquor as well as formed during evaporation) left the evaporator (or the concentrated liquor). This indicates that most of the methanol in the weak liquor will end up in the condensate and more methanol will be found in the condensate than those originally in the weak black liquor. It should be pointed out that both the evaporator and the evaporation condition (atmospheric pressure) in this study are different from black liquor evaporation in mills. The 300% increase in methanol formation was obtained in laboratory conditions. We believe that the evaporation of methanol rapidly removes the product from the evaporator that could enhance the lignin demethylation reaction. The remove of water due to

evaporation also increases the lignin and OH concentration in the liquor. Further study using pilot scale evaporator needs to be carried to simulate mill black liquor evaporation. Research also need to be carried out to investigate the partition and formation of other VOCs during evaporation and the effect of further concentration (high solids) on methanol formation.

SUMMARY

We conducted laboratory pulping, black liquor storage and evaporation studies to understand the methanol formation in pulp mills. We found that methanol formation during pulping is mainly from xylan hydrolysis reactions. The effect of pulp kappa number on methanol formation is a result of ongoing xylan hydrolysis and lignin demethylation. The effect of the pulping process on final methanol formation is not significant. The final methanol formed for bleach and liner board grade of southern pine pulps are about 8.5 and 7.0 kg/ODT pulp, respectively.

Methanol can also be formed in black liquor storage and evaporation through the slow reaction of lignin demethylation. This study indicates that methanol formation is significant in black liquor storage under mill operation conditions. Both temperature and lignin content in the liquor can affect methanol formation in storage. Based on laboratory evaporation study, a very significant amount of methanol will be produced during liquor concentration. Most of the methanol will leave the concentrated liquor and can be collected in the condensate.

ACKNOWLEDGEMENT

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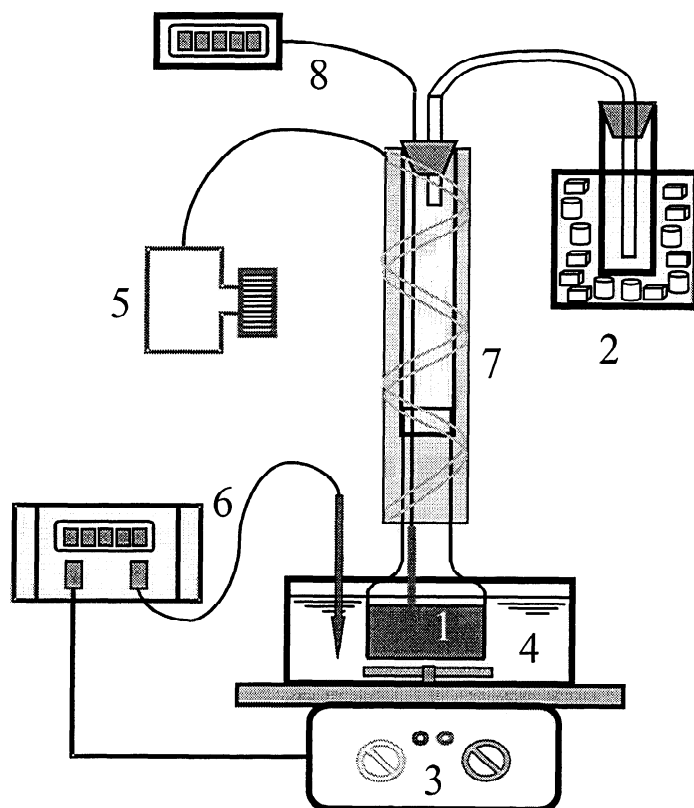
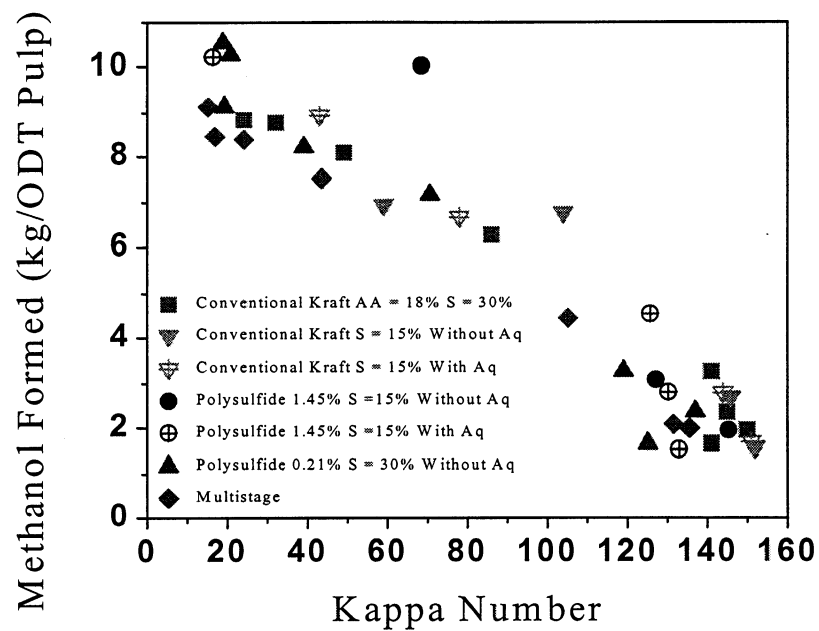


Fig. 1 Schematic of the laboratory batch evaporator. (1) Boiler and black liquor, (2) condensate receiver, (3) heating plate, (4) isothermal bath, (5) heater, (6) thermocouple and temperature controller, (7) distillation column and heating tape, (8) thermocouple.

(a)



(b)

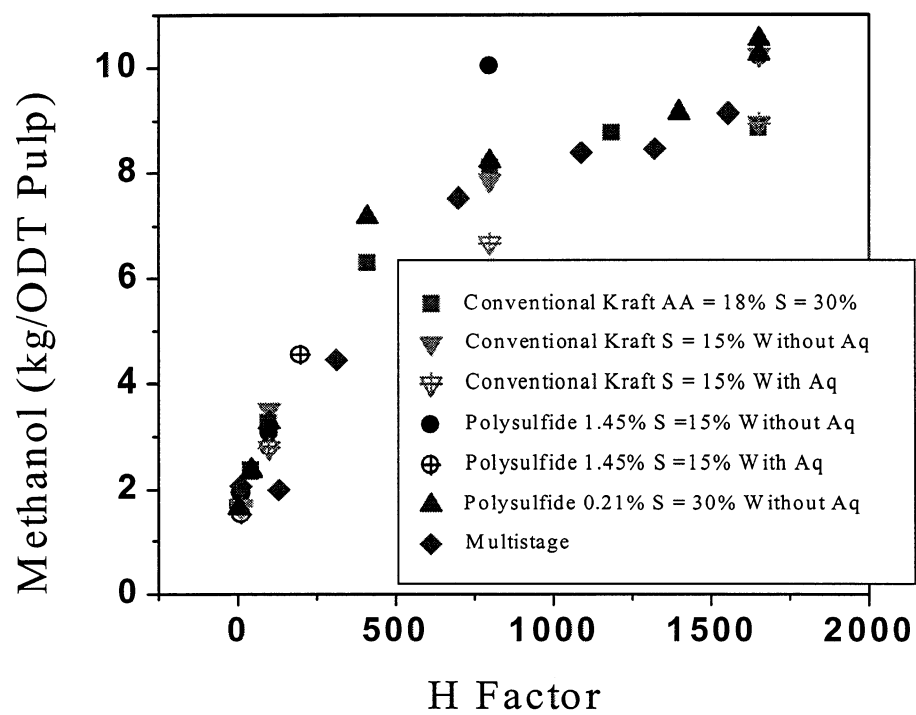


Fig. 2 Effects of kappa number (a) and H factor (b) on methanol formation in various pulping processes.

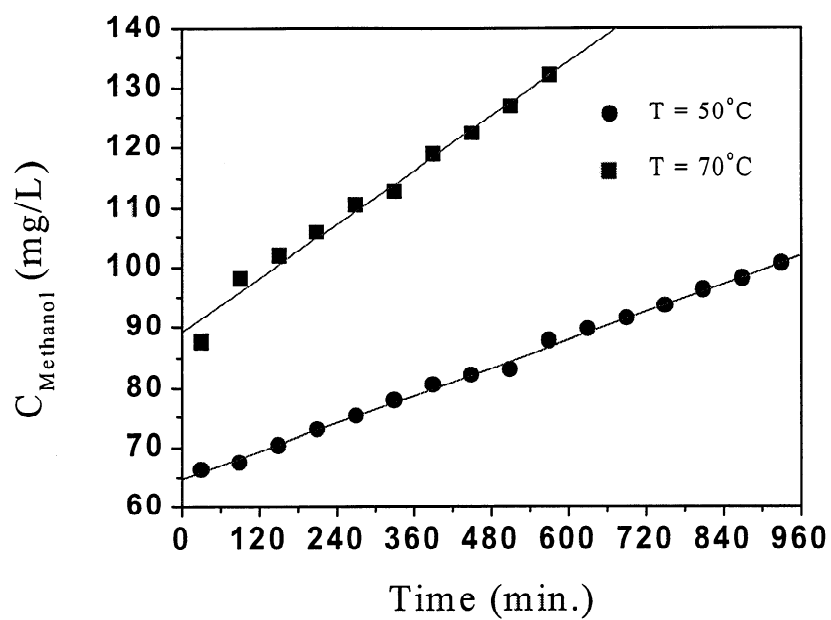


Fig. 3 Methanol formation data obtained in a caustic solution with alkali lignin in an isothermal container.

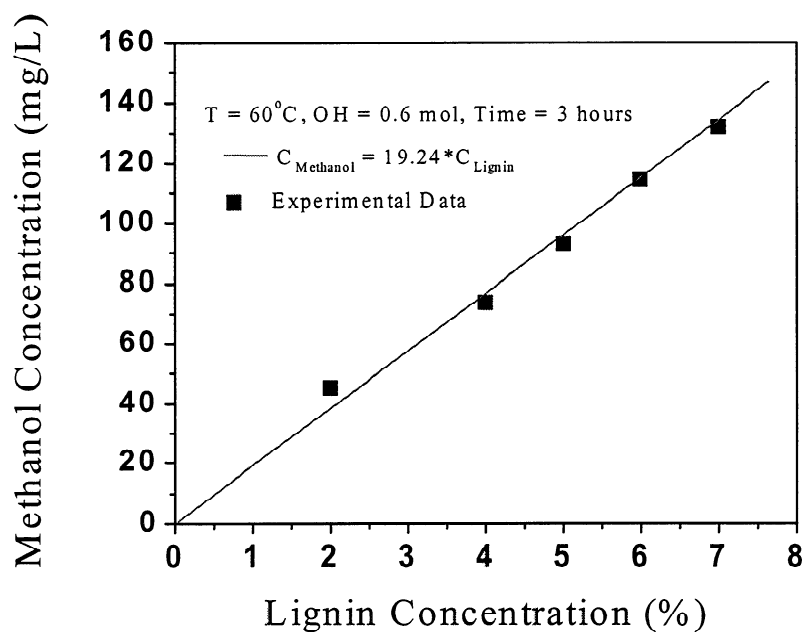


Fig. 4 Effect of lignin mass concentration on methanol formation in a caustic solution.

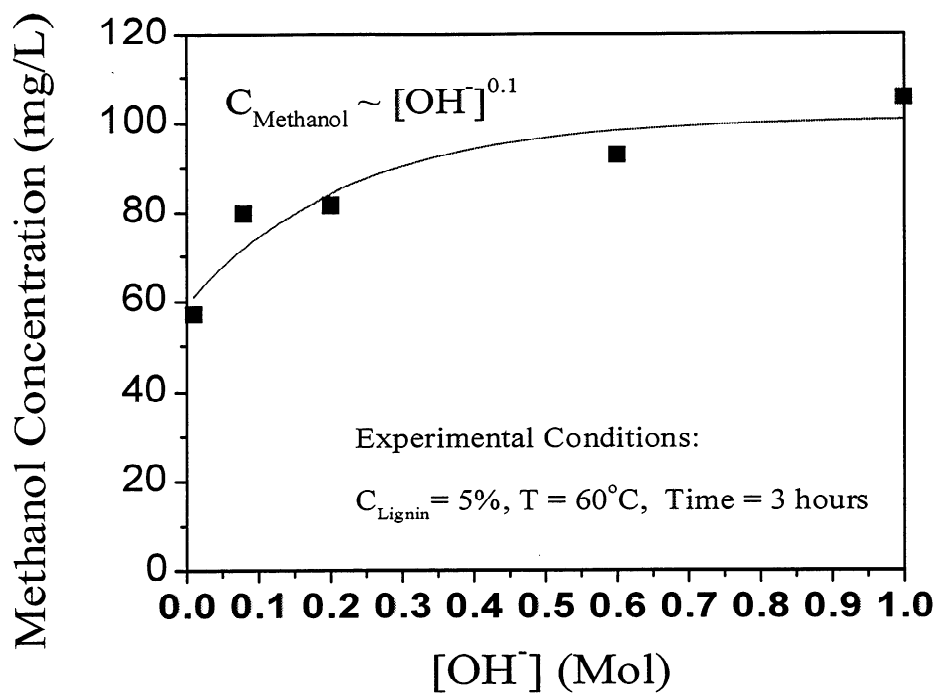


Fig. 5 Effect of hydroxide concentration (or pH) on methanol formation in a caustic solution with lignin.

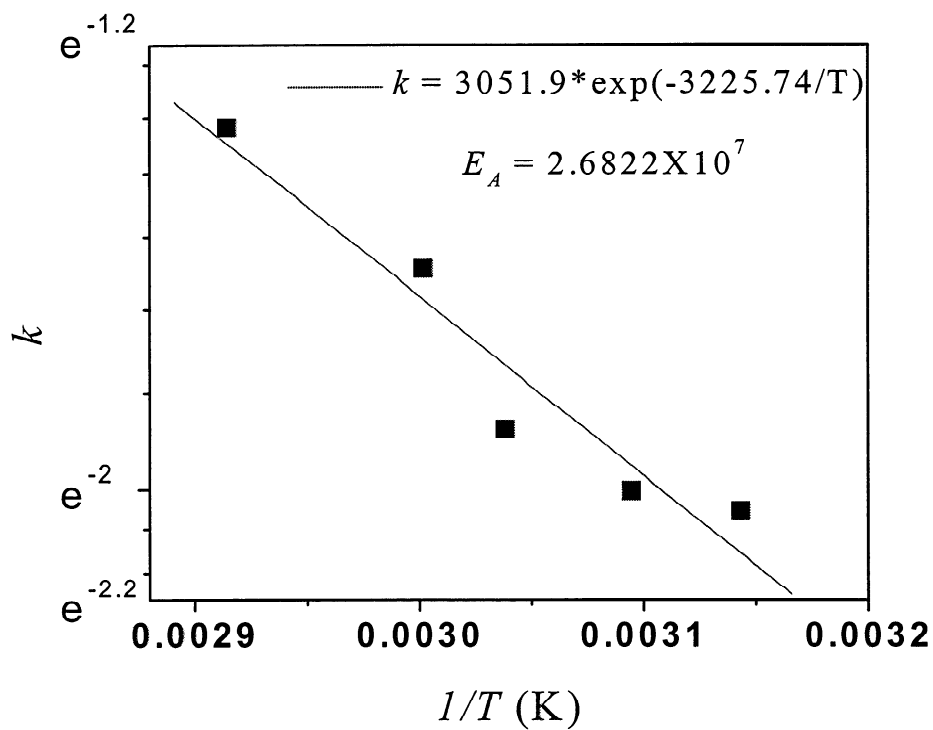


Fig. 6 Arrhenius plot of methanol formation reaction rate constant in a lignin caustic solution.

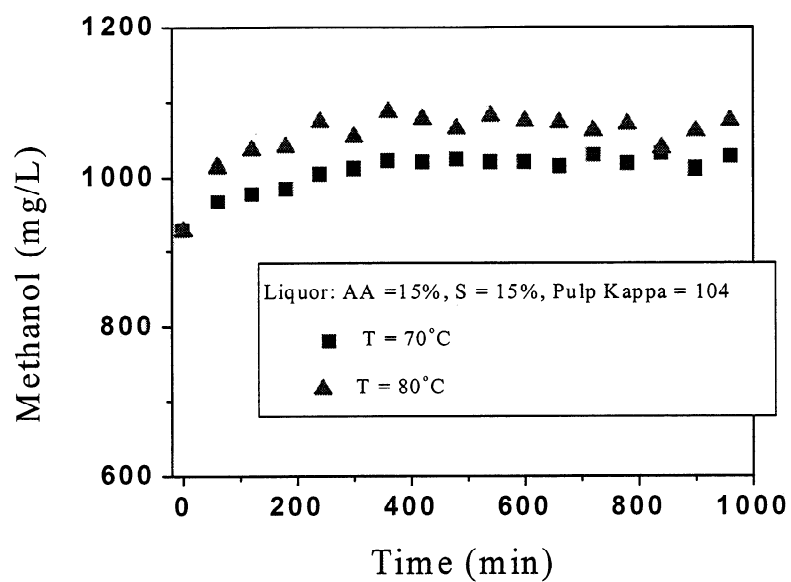


Fig. 7 Effect of temperature on methanol formation in black liquor storage.

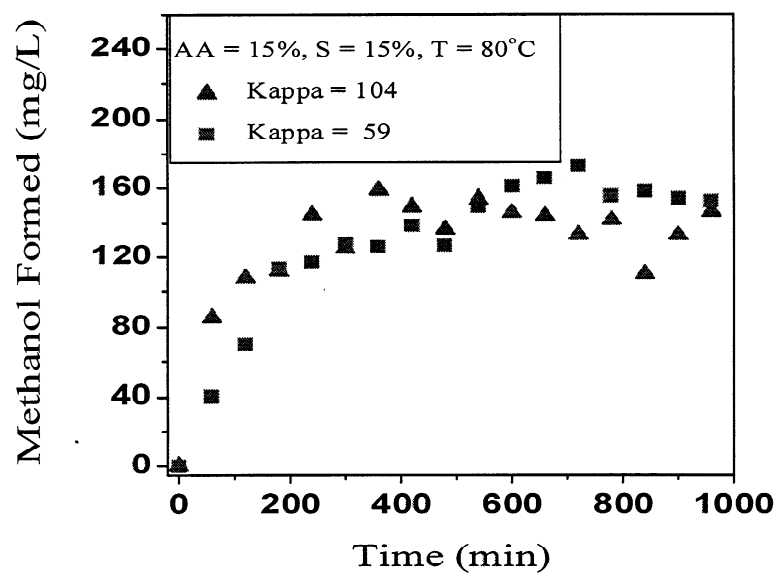


Fig. 8 Effect of pulping kappa number on methanol formation in black liquor storage.

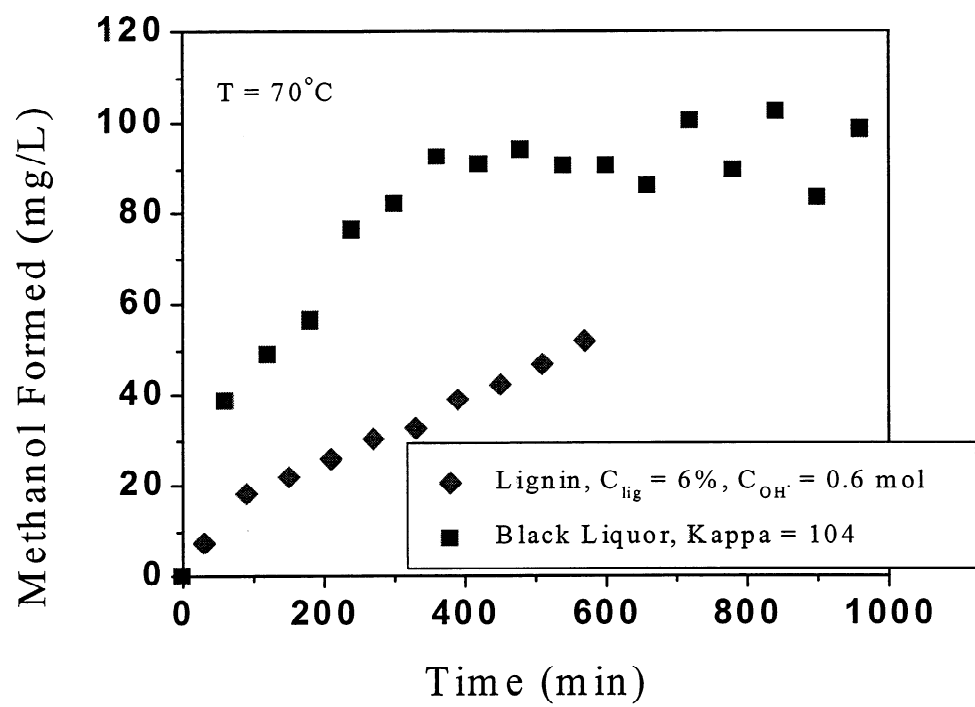


Fig. 9 Comparison of methanol formation rates in a lignin caustic solution vs. in a kraft black liquor.

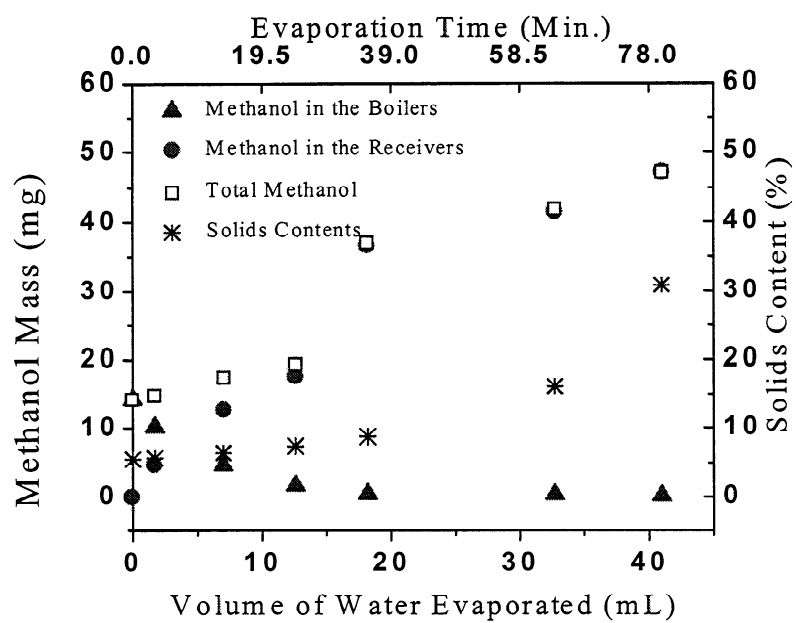


Fig. 10 Methanol formation in laboratory batch evaporation of a kraft mill liquor.

